LIFE WBRM PROJECT

CONTENTO TRADE SRL

Technological innovation for the environment

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"WBRM" - Waste based reinforced materials

BRIEF DESCRIPTION:

Partners:

Contento Trade srl, Campoformido, Italy
Stazione Sperimentale per il Vetro, Murano, Italy
CTG Spa - Italcementi Group, Bergamo, Italy
Institute Textile de France, Ecully, France
KEMA, Utrechtseweg, Arnhem, Netherlands

OBJECTIVES:

This is a demonstrative project that intend to test, at pilot scale, the production processes of new typologies of fibres useful for the textile and non woven fabric production and for the cement, plastic and bitumen based reinforcement products. The proposed project aims to transform mixtures of municipal waste incinerator ashes (MWI ashes), coal combustion ashes and steel making dusts (SM) in long glassy fibres with good mechanical strength and high chemical resistance.

The most important aims of the project are:

- ✓ The demonstration of industrial validity of the fibre production process, thanks to the non - stop production at pilot scale strictly monitored;
- ✓ The punctual determination of the chemical, physical and mechanical characteristics of the new fibres and of their production cost;
- ✓ The control of the process adaptability to the different MWI ashes (from municipal wastes) existing in Europe;
- ✓ The execution of an environmental evaluation (LCA) of the new fibres to underline the advantages linked to their use;
- ✓ The production and the characterization of the finished products made with the new fibres, underlining the potentialities of the proposed technology and its versatility also as finished product.

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STATE OF THE ART

Glassy combustion residues (coal and incinerator ashes).

Many aspects of the glassy combustion residues have been studied for different purposes: improvement of the combustion processes, environmental impact, their application in function of their properties. So for this reason a remarkable technological background in many sectors has been realized.

The chemical and physical properties of the coal combustion residue (fly ashes, bottom ash, gasifier slag) are well documented and variations depend mainly on the type of coal burned and the combustion technique used. Because of precipitation of initially volatilized elements on the surface of the solidified ash particles, the structure of fly ash consists normally of an exterior reactive shell on the main Si-Al interior glass matrix. This shell contains the majority of the environmental-threatening elements as Se, As, Cd, Mo, Zn, Sb, V, Cr and S.

The MWI residues are much less homogeneous and less vitrified compared to the coal residues. This is caused by the variation of the burned material and by the relatively low combustion temperature (+850°C).

Standardized leaching and diffusion tests determine the environmental quality of those residues in granular and bulk form. The European Technical Committee CEN292/WG2 is actually developing EU norms on this matter.

Following the norms, the critic elements for the utilization of glassy combustion residues are:

- ✓ Coal residues: Mo, Se, Sb, V, Ba, As
- ✓ MWI residues: Mo, Cu, Pb, Sb, Cd, Se, Zn, S, Cl.

Traditionally, glassy combustion residues are applied in various building materials and civil engineering constructions. This application can roughly be divided into "bound" and "bulk" use. In bound form the glassy residue is embedded in a matrix of different material and interaction between the glassy residues is integrally applied for filling and construction. The technique involved may also be described as "addition to other materials" or "replacement of other materials".

A number of these applications have been investigated world-wide, and some have been established and belong to common practice (reason why no specific references are cited).

Bound form:

- ✓ additives in cement and concrete
- ✓ brick fabrication
- ✓ fabrication of artificial dimension stone (ardelite)
- ✓ manufacturing of refractive materials
- ✓ additives and replacement in ceramics

Bulk from:

- ✓ road and rail construction and pavement bulk material
- ✓ back-filling in mining operations
- ✓ soil improvement

New products and applications:

A number of techniques adopted from different disciplines have been and are still being investigated in order to either improve the environmental quality of the glassy residues or to make higher quality products out of glassy residues. The most important are:

Grinding and milling techniques

The micronisation of fly ash into a ultra-fine product (1um) has been investigated by a great number of researchers. Although milling costs are high (+ECU200/t), the products have high added values and may complete with expensive raw materials such as silica fumes, because of their ability to improve concrete strength considerably.

Separation techniques

Mineral processing techniques such as magnetic, electrostatic and floating methods have been successfully used to remove certain particles (Fe oxides, un burnt carbon) from coal residues. Only the removal of un burnt carbon has been developed on industrial scale. Because MWI residues have more appropriate structure and metal distribution, magnetic, heavy liquid and eddy current separators are commonly found at to extract iron, steel and non ferrous metals.

Extraction techniques

Forced leaching, with and without addition of reagents, has been investigated in order to remove the leachable elements, thus reducing initial leaching and

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improving the environmental quality. The aim is to produce a clean residue that meets the environmental standards and could be utilized for applications so far excluded because of the content of trace elements/i.e functional fillers. Using selective soluble complexing agents, large portions of the environmentally problematic elements (Mo, Se, Sb, As) could be removed. (13) The main drawback is the amount of solutions to be cleaned and the incomplete de-watering of the product. This can be overcome by using volatile complexants (SERVO system, UHERTS, supercritical CO2, UCC), a novel method for the recovery of metals from certain ores, which also have potential for treatment of certain waste stream and reclamation of polluted land. These methods are now tested for their application in environmental technology and to apply to combustion residues as well.

Conversion of glassy residues into useful minerals

The glassy residues provide a source of Al and Si, which forms the bulk of zeolite composition. In an alkaline environment (addition of hydroxide solutions), fly ash can indeed be converted into zeolite. The conversion of fly ash onto zeolitic materials has been reported for more than 20 years, mainly from European and Asian researchers. The adsorption capacity of tailor-made fly ash zeolites exceeds that of the main commercialized natural zeolites and the ion specificity is much higher. Vice versa, commercial zeolites synthesized from pure chemicals show better performance but are much more expensive. Therefore, fly ash zeolites are expected to compete with the lower range of artificial zeolites for bulk applications such as in detergents, water purification and waste immobilization.

Immobilization and vitrification techniques

Cold and hot immobilization techniques are used to fix mobile elements and thus improve the environmental quality of glassy combustion residues. Cold immobilization implies the physical or chemical fixing through additions of reactive materials (i.e. cement or lime). Hot immobilization techniques (sintering and vitrification) fix and homogenize these elements in a glassy structure. Because of the high energy costs involved, such processes many only be considered for highly polluted residues (nuclear waste, MWI fly ash).

Recovery of metals

The recovery of several metals from fly ash has been studied, Technically, fly ash can be used as an alternative source of aluminum, but is not competitive with traditional bauxite sources. Also iron and silicon and vanadium can be recovered. Other metals such as germanium and gallium were recovered from

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typically high Ge-Ga-gly ash. Vanadium and nickel are also successfully recovered from Orimulsion ash (BRE CT92 0120).

Other uses

In countries with a long mining history, fly ash mixtures are applied for the stabilization of (old) mine workings. The construction of artificial reef for fishery using combustion residues is a remarkable activity, running a EC funded European Artificial Reff Research Network.

Sorbent agents for flue gas de-sulphurization are being developed as well as fire-proof construction materials. Further, the Limerick University is carrying our research into the development of polyalkenoate-cements from gasifier slag. The development of ettringite-based binders from glassy combustion residues is supported by researches made by Contento Trade and Mitsui Babcock Energy ltd.

Steel making dusts

Also the steel making dusts (SM dust) represent an environmental important problem all over the Europe and all over the world.

The use of steel scraps zinc coated or coated with lead based paints as raw matters for the production of steel and iron alloys strongly increases the content of heavy metals as zinc and lead in the fumes that, after filtration are transformed in dust or mud that are wastes difficult to dispose.

It must be underlined that the production of EAF steel is continuously increasing; in fact it's possible to foreseen that the annual increasing on world scale will be about 5%, principally caused by the substitution of the production with oxygen furnaces.
The previsions, in fact, tells that the sector of the oven electric production will increase from 33% of 1995 to 50% of 2010, and consequently the production of EAF steel should increase from the 246 million ton/year of 1995, to 300 million ton/year in 2000, till about 400 million tons/year in 2005. All the SM dust contains big amounts of oxides of zinc, lead, manganese and cadmium oxides, variously combined with iron, silica, alkaline and earth-alkaline metals. There are, moreover, also anionic compounds as chlorides, phosphates and sulphates.

On the basis of a statistical research developed by Contento Trade in 1996 it's possible to give some information on the concentration of polluting agents in Sm dusts from EAF:

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	Maximum concentration	Minimum concentration	Average content referred to SM dust produced
ZnO	40 %	10 %	26,53 %
PbO	10 %	1 %	5,32 %
CdO	0,1 %	0,04 %	0,08 %

In the dusts deriving from the oxygen furnaces the medium content of heavy metal is reduced at less than half because the raw matter is made principally by iron ore and not by steel scraps.

There are many processes that have been studied till now for the heavy metals recovery existing in the SM dusts: they are based on pirometallurgic methods (Waelz, plasmazinc, etc.), hydrometallurgic mehods (Zincex, Ezinex, etc.) or comination of those two. The most diffused method in Europe is the Waelz process that is based on the treatment at high temperature (1200-1300°C) of the dusts in reducing atmosphere with specific additives.

The hydro-metallurgic methods are based on the use of chemical (strong acids or alkali) to solubilize the heavy metal available as oxides, followed by cementation treatments to purify the metallic solutions and by electro winning o obtain metallic agglomerates from the solutions. The combination of the above used methods are substantially hydro-metallurgic methods, where the initial solutions phase is helped with opportune thermal treatments. All the treatments at present available for these typologies of residues produce a lot of wastes, sometime dangerous, sometimes in quantities greater than the amount of treated residues and they need notable plant investments.

The processes that now have been developed till the industrial phase are not economically self-sufficient and need some financial support from the producer SM dusts. Moreover, all the processes need considerable content of heavy metal (at least 20% by weight of ZnO) not to lose their economic credibility.

Many SM dust from Electric Arc Furnace and quite all the ones coming from oxygen furnaces don't reach this limit: for this reason and because of the strong incidence of the transport costs of the residues to the recycling plants, the most used treatment method for this typologies of wastes is landfilling.

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MAIN INNOVATIONS

The main innovation of the project regards, on one hand, the production of high quality, high added value vitreous fibers from wastes by means of a new and clean technology and, on the other, the possibility of an alternative route for ash recycling, especially for the whole MWI amount, at a much lower environmental cost respect to the methods at present available on the market.

The fibers obtained from wastes with this new technology have very good characteristics as:

- ✓ the presence of heavy metals as zinc and iron in the glassy structure improve the chemical stability of the obtained fibers, creating a real protective coat that reduce the velocity of the alkali silicate reaction, increasing the durability of the obtainable fiber reinforced cement;
- ✓ the presence of heavy metal oxides may lead to an improvement of adhesion of the fibers with the polymeric matrix used in the composite industry (thermoset resin like polyester or thermoplastic resin like polypropylene or polyamide);
- ✓ the presence of metal compounds may also affect the electrical properties (low resistively) and lead to higher thermal conductivity of the fibers.

Other innovative actions will also regard the spinner device:

new ceramic materials studied for the particular purpose, different from the traditional but very costly platinum, will be tested to reduce the incidence of the maintenance costs on the price of the produced fibers.

Finally the global approach towards the problem of the MWI ash management is itself innovative, because besides the complete elimination (by combustion) of the polluting organic fraction and the recovery of the anionic fraction (chlorides and sulphates) that can be valorized in the aluminum industry, reusing the heat wasted during the fibers production process. In this way it's possible to save raw material and resources in different industrial sectors, it's possible to optimize the energy consumption, to minimize the emissions in the environment: it's without a doubt an innovative cleaner technology.

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